

FORM PTO-1390 (Modified)
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

6272-0049-0 PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/554090

INTERNATIONAL APPLICATION NO
PCT/EP98/07290INTERNATIONAL FILING DATE
13 NOVEMBER 1998PRIORITY DATE CLAIMED
25 NOVEMBER 1997

TITLE OF INVENTION METHOD FOR PRODUCING WATER-SOLUBLE OR WATER-SWELLABLE
POLYMERIZATES WITH A VERY LOW RESIDUAL MONOMER CONTENT, PRODUCTS PRODUCED
ACCORDING TO THIS METHOD AND THE USE THEREOF

APPLICANT(S) FOR DO/EO/US

Miroslav CHMELIR, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report
Notice of Priority

U.S. APPLICATION NO. IF KNOWN, SEE 37 CFR

09/354090

INTERNATIONAL APPLICATION NO.

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20. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☒ Search Report has been prepared by the EPO or IPO **\$840.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) **\$670.00**
- ☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) **\$760.00**
- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$970.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) **\$96.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =**CALCULATIONS PTO USE ONLY****\$840.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

\$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	

TOTAL OF ABOVE CALCULATIONS = \$970.00

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).

☐**\$0.00****SUBTOTAL = \$970.00**

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).

+

\$0.00**TOTAL NATIONAL FEE = \$970.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐**\$0.00****TOTAL FEES ENCLOSED = \$970.00**

Amount to be:	\$
refunded	
charged	\$

☒ A check in the amount of **\$970.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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REGISTRATION NUMBER

DATE

May 24, 2000

09/554090

527 Rec'd PCT/PTO 24 MAY 2000

6272-0049-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

MIROSLAV CHMELIR ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW US PCT APPLICATION :
(Based on PCT/EP98/07290)

FILED: HEREWITH :

FOR: METHOD FOR PRODUCING WATER-
SOLUBLE OR WATER-SWELLABLE
POLYMERIZATES WITH A VERY
LOW RESIDUAL MONOMER
CONTENT, PRODUCTS PRODUCED
ACCORDING TO THIS METHOD
AND THE USE THEREOF

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please cancel Claims 1-11.

Please add the followings claims:

09/554090

--12. A process for producing water-soluble or water-swellaable synthetic polymer products by free-radical polymerization in aqueous solution of acrylic acid and/or acrylic acid derivatives partially or completely neutralized with basic nitrogen compounds, wherein exceedingly low residual monomer levels are achieved by subsequent heating of the polymer products at a temperature of from 120 to 240°C.

13. The process according to claim 12, wherein said nitrogen compound is selected from the group consisting of ammonia, ammonium hydroxide, hydroxylamine, alkanolamines, alkylamines and mixtures thereof.

14. The process according to claim 12, wherein said nitrogen compound is selected from the group consisting of ammonia, ammonium hydroxide, mono-ethanolamine and di-ethanolamine.

15. The process according to claim 12, wherein the acid monomer component is neutralized with said nitrogen compound up to a neutralization level of from 10 to 100%.

16. The process according to claim 12, wherein monomers based on acrylic acid, methacrylic acid or derivatives of these carboxylic acids are subjected to polymerization,

17. The process according to claim 12, wherein monomers based on homo- or copolymers of acrylic, methacrylic acid, acrylamidopropanesulfonic acid, alkali or ammonium salts of these carboxylic acids, of acryl- or methacrylamide and derivatives thereof, of vinylpyrrolidone, and as copolymers of each other, or are used with other, only partially water-soluble monomers are subjected to polymerization

18. The process of Claim 12, wherein said partially water-soluble monomer is vinyl acetate.

19. The process according to claim 12, wherein at least one crosslinker based on a bi- or polyfunctional monomer is used in addition.

20. The process according to claim 12, wherein the polymer product is heated at a temperature of from 140 to 180°C.

21. The process according to claim 12, wherein polymer products having a content of residual monomer of less than 50 ppm are formed.

22. The process according to claim 12, wherein polymer products having a content of residual monomer of less than 30 ppm are formed.

23. The process according to claim 12, wherein polymer products having a residual content of acrylamide of less than 10 ppm are formed.--

REMARKS

Claims 12-23 are active in the present application. Support for Claims 12-23 is found in Claims 1-11 and the specification as originally filed. No new matter is believed to have been introduced by the amendments submitted above.

Applicants submit that the present application is now in condition for examination on the merits. Early notice of such is earnestly solicited.

Respectfully submitted,

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**METHOD FOR PRODUCING WATER-SOLUBLE OR WATER-SWELLABLE
POLYMERIZATES WITH A VERY LOW RESIDUAL MONOMER CONTENT,
PRODUCTS PRODUCED ACCORDING TO THIS METHOD AND THE USE THEREOF**

The invention relates to a process for producing synthetic polymers based on acrylic acid and derivatives thereof, which polymers have an exceedingly low content of residual monomers. The polymers have high molecular weights and either are water-soluble or have high absorptive capacity for water, aqueous solutions and body fluids.

Various synthetic polymer products having absorptive capacity for water and body fluids have been described in numerous patents: e.g. crosslinked polymers and copolymers based on acrylic or methacrylic acid (US 4,018,951, US 4,066,583, US 4,062,817, US 4,066,583, DE-OS 26 13 135, DE 27 12 043, DE 28 13 634), or acrylamidopropanesulfonic acid copolymers (DE 31 24 008). These absorbents are virtually insoluble in water, absorbing a multiple of their weight of water, urine or other aqueous solutions at equilibrium. In addition to high absorptive capacity, other properties of synthetic absorbents such as low residual monomer content, low ratio of water solubles and high gel strength of the swollen polymer particles are also mentioned in some patent specifications.

In the production of high molecular weight water-soluble or water-swellaable, i.e., partially crosslinked polymers and mixed polymers, complete conversion of the monomers - in particular, monomers based on acrylic acid - has been found impossible. On an industrial scale, residual monomer levels of from 0.1 to 0.5 wt.-% normally are observed in the polymer product.

The toxicity of the monomers remaining in the polymer product is well-known and therefore, a process for producing polymers and mixed polymers virtually free of monomers would be highly convenient. Up to now, since it has not been possible as yet to conduct a polymerization process in such a way that virtually no residual monomers would remain, it has been attempted to remove the toxic residual monomers from the polymer product by converting them into harmless derivatives. Thus, DE-AS 1,070,377 and US 2,960,486 use mixing the aqueous solutions of high molecular weight acrylamide polymers with sodium disulfite solution and drying at 80-120°. One precondition for these methods is processing the polymer product in a highly diluted (2-3%) polymer solution, which is uneconomic, and for this reason these methods have rarely been applied in practice.

The treatment of a polymer gel with an aqueous solution of sodium bisulfite or metabisulfite has been described in US 3,755,280, and with a solid alkali sulfite in EP 175,554, where residual monomer contents of from 0.03 to 0.3 wt.-% have been obtained. Likewise, the JP-PS 56/103207 uses bisulfites, sulfites and pyrosulfites for the same purpose. US 3,780,006 uses gaseous sulfur dioxide in order to decrease the acrylamide concentration in an emulsion polymer. EP 505,163 uses treatment of polymer products with a combination of metabisulfite and a surface-active agent (HLB from 3 to 40) subsequent to completed polymerization, thereby decreasing the residual monomer content down to 10 ppm. From 2 to 5 wt.-% of metabisulfite (relative to the polymer gel having 40% w.s., that is, from 5 to 12.5 wt.-% of metabisulfite relative to the dry polymer product) is necessary in such a secondary treatment of polymer gels in order to achieve the desired decrease in residual monomers. Such high quantities of added substances may have highly negative effects on the application-technical properties.

EP 303,518 A2 describes a process for producing absorbent polymer products based on acrylic acid/acrylamide, and according to this invention, a high degree of neutralization of from 70 to 100 mole-%, a high monomer concentration of at least 50%, and a combination of thermally decomposing azo and redox initiators are used. Owing to these conditions, the reaction proceeds in such a way that all of the water used in the batch undergoes vaporization even during the polymerization, so that subsequent drying can be omitted, and the residual monomer contents are said to drop below 500 ppm, preferably below 200 ppm. The residual monomer levels of the experimental examples have not been specified.

DE 37 24 709 A1 describes a process for producing polymer products having low residual monomer content, wherein the polymer products following production are reacted in a swollen form as a gel or in solution with compounds reacting with the double bonds in the residual monomers at 50-150°C.

In US 4,766,173, the decrease of acrylic acid residual monomer in polymer products is effected by subsequent treatment of the polymer products using amino acids of the lysine and cysteine types at temperatures from 80°C on.

WO 94/20547 describes additives such as bromate and chlorate in the polymerization solution and subsequent heating of the final polymer wherein, *inter alia*, a decrease of the residual monomers is effected by the additives. The bromates and chlorates may also be added subsequent to the polymerization. Despite these measures, the residual monomer content of the polymer products is between about 135 and 1100 ppm.

While the prior art processes described above permit a substantial decrease of residual monomers, they involve several drawbacks such as malodors as a result of liberated sulfur dioxide, corrosion of the plant by sulfur oxide resultant products (e.g. sulfurous acid and sulfuric acid as well as salts thereof in acidic medium). Above all, however, any subsequent treatment of the final polymer that has been produced represents an additional technological step necessitating additional apparatus and a quite considerable input of time, and also, a quite significant amount of additive remains in the final product and may adversely affect the application-technical properties.

It is therefore the object of the invention to produce synthetic polymer products of *per se* known chemical composition with high molecular weight or high retention capability for water, aqueous liquids and body fluids, using particular specific conditions so as to obtain final products having an extremely low residual monomer content and good application-technical properties, without necessitating a subsequent treatment of the produced polymers using additional chemical compounds.

Surprisingly, it has now been found that synthetic polymer products based on acrylic acid and having the desired properties and an extremely low content of residual monomers can be produced by free-radical polymerization in aqueous solution, provided at least one basic nitrogen compound such as ammonia is used in the partial or complete neutralization of acid monomer components during the preparation of the monomer mixture to be polymerized, and the polymer products are subjected to subsequent heating at 120 to 240°C, preferably 140 to 180°C. The polymer products according to the process of the invention have an extremely low content of residual monomers, preferably being below 50 ppm, particularly below 30 ppm. Of special importance is

the fact that acrylamide, which is rated critical in toxicological terms, can be decreased to a residual content of below 10 ppm.

For example, ammonia or ammonium hydroxide, aliphatic mono- and polyamines, particularly aliphatic C₁-C₁₀ amines, cycloaliphatic mono- and polyamines, particularly cycloaliphatic C₆-C₁₂ amines, aromatic mono- and polyamines, particularly aromatic C₆-C₁₂ amines, heterocyclic amines, hydroxylamine and alkanolamines such as monoethanolamine and diethanolamine or mixtures thereof are used as basic nitrogen compounds for neutralization. Particularly preferred nitrogen compounds are ammonia or ammonium hydroxide, ethanolamine and diethanolamine.

The nitrogen compounds for complete or partial neutralization of the acid monomer components can be employed in the form of their free bases. In this context, part of the acid monomers may also be neutralized by other bases, and the nitrogen compound may be present in a molar deficit relative to these other bases. Advantageously, the nitrogen compound for neutralizing the acid monomer component can be used for neutralization levels ranging from 10 to 100%.

In order to achieve an economic production of the polymers, the polymerization is carried out using initiators which decompose at relatively low temperatures. Inorganic or organic peroxides or redox systems are used as common initiators. When polymerizing in aqueous phase, inorganic peroxides such as peroxodisulfates are frequently used alone or in combination with a reducing component.

The polymerization can be initiated using a redox initiator system or by means of photopolymerization. The redox initiator system mostly consists of two components, i.e., an inorganic or organic peroxide-containing compound

and a reducing component such as sulfite, hydrosulfite, thiosulfate, sulfinic acid, ascorbic acid and their copper, ferrous or manganese salts. Alkali metal or ammonium peroxides such as potassium peroxodisulfate and hydrogen peroxide can be used as inorganic peroxide compounds, and benzoyl peroxide, butyl hydroperoxide as organic peroxides. In general, the polymerization is initiated using a redox initiator system. Other initiators may be used in addition to such an initiator system. In the case of photopolymerization which can be initiated by UV-containing light, so-called photoinitiators like e.g. benzoin or benzoin derivatives such as benzoin ethers, benzil and derivatives thereof such as benzil ketals, acrylic diazonium salts, azo initiators such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-amidinopropane) hydrochloride or acetophenone derivatives are used. The amounts of peroxide-containing component and reducing component may range from 0.0005 to 0.5 wt.-%, preferably from 0.001 to 0.1 wt.-% (relative to the monomer solution), and the amounts of photoinitiators may range from 0.001 to 0.1 wt.-%, preferably from 0.002 to 0.05 wt.-% (relative to the monomer solution).

Predominantly, possible monomers are acrylic acid, acrylamide, methacrylic acid, and methacrylamide, which are polymerized to form homopolymers or mixed polymers, but also other monomers such as acrylonitrile, methacrylonitrile, N,N-dimethylacrylamide, vinylpyridine, vinyl acetate, as well as other water-soluble polymerizable acids and salts thereof, particularly maleic, fumaric, itaconic, vinylsulfonic, or acrylamidomethylpropanesulfonic acid; also, hydroxy group-containing esters of polymerizable acids, particularly the hydroxyethyl and hydroxypropyl esters of acrylic and methacrylic acid can be used; furthermore, amino group-containing and ammonium group-containing esters and amides of polymerizable acids, such as dialkylamino esters, particularly the dimethyl and diethylaminoalkyl es-

ters of acrylic and methacrylic acid, as well as trimethyl and trimethylammoniumalkyl esters and the corresponding amides. The above monomers can be polymerized alone to form homopolymers or mixed with each other to form mixed polymers. In addition, small amounts of water-insoluble monomers can be copolymerized with the above monomers, e.g. esters of acrylic and/or methacrylic acid with C_1 - C_{10} alcohols, styrene and alkylated styrenes. In general, the proportion of water-soluble monomers is from 60 to 100 wt.-%, relative to the overall monomers. As a rule, the water-insoluble (hydrophobic) monomers make up for 0 to 40 wt.-% of the monomers.

Small amounts of crosslinking monomers, e.g. monomers having more than one reactive group in their molecule can be polymerized together with the above-mentioned monomers, thereby forming partially crosslinked polymer products which are no longer soluble in water but merely swellable. Bi- or multifunctional monomers, e.g. amides such as methylenebisacrylamide or -methacrylamide or ethylenebisacrylamide, and also, esters of polyols and alkoxyated polyols, such as diacrylates or triacrylates, e.g. butanediol or ethylene glycol diacrylate, polyglycol di(meth)acrylates, trimethylolpropane triacrylate, di- and triacrylate esters of trimethylolpropane preferably oxyalkylated (ethoxylated) with 1 to 30 mol alkylene oxide, acrylate and methacrylate esters of glycerol and pentaerythritol, or of glycerol and pentaerythritol preferably oxyethylated with 1 to 30 mol ethylene oxide, and also, allyl compounds such as allyl (meth)acrylate, alkoxyated allyl (meth)acrylate preferably reacted with 1 to 30 mol ethylene oxide, triallyl cyanurate, diallyl maleate, polyallyl esters, tetraallyloxyethane, triallylamine, tetraallylethylenediamine, allyl esters of phosphoric acid or phosphorous acid, and crosslinkable monomers such as N-methylol compounds of amides such as methacrylamide or acrylamide

and ethers derived therefrom may be mentioned as crosslinking monomers. The ratio of crosslinking monomers is from 0 to 10 wt.-%, preferably from 0.01 to 3.0 wt.-%, relative to the overall monomers.

The water-absorbing polymeric absorbents are obtained using at least one crosslinker. As crosslinkers, those compounds are used which contain at least 2 or more functional groups (double bonds, epoxy groups) and are capable of being incorporated into the growing polymer chains during polymerization. As a result, crosslinking sites are formed at various positions in the polymer product, which hold together the individual polymer chains, taking such an effect that the polymer particles can merely swell in a liquid and will not dissolve in said liquid. The properties of the crosslinked polymer are determined by the chemical structure of the crosslinker, the number of crosslinking sites, but also, by their distribution in the polymer chains. In case of optimum incorporation of crosslinker into the polymer, crosslinked polymer products will be formed having their crosslinking sites uniformly distributed, so that non-crosslinked regions or even non-crosslinked (i.e., water-soluble) low molecular weight components are barely present in the polymer product. Uniform distribution of the crosslinking sites within the polymer results in a product which also has optimum retention capability for aqueous liquids and optimum gel strength in the swollen state.

The polymerization preferably is performed in aqueous solution, batchwise in a polymerization vessel or continuously on a continuous belt, e.g. according to DE 35 44 770. Given a virtually adiabatic course of polymerization, an aqueous polymer gel is formed at a corresponding initial concentration of from 15 to 50 wt.-% of monomers. By selecting the initial monomer concentration and an ap-

appropriate low initial temperature ranging from 0 to 50°C, preferably from 5 to 25°C, it is possible to conduct the polymerization in such a way that the maximum temperature in the aqueous polymer gel being formed can easily be controlled.

According to the process of the invention, the produced polymer is heated at a temperature of 120-240°C, preferably 140-180°C in order to achieve said low residual monomer content. Care must be taken not to deteriorate other essential properties of the polymer product by an excessively high temperature or long time. The optimum time required for heating depends on the nitrogen compound concentration and temperature level and can be determined using just a few experiments. In most of the cases, a time period between 10 minutes and 2 hours is sufficient, preferably between 10 minutes and 1 hour.

The polymer products are classified in screen fractions required for various applications. For example, when using the crosslinked polymer products as absorbents in the hygiene sector, grain size distributions of from 0.2 to 1 mm are preferred, products ranging from 0.2 to 3 mm are preferably used in the agricultural sector, and products ranging from 0.1 to 1.2 mm for soluble polymers in the flocculant sector.

As a result of the low content of residual monomers, the polymer products according to the invention have the following advantages over well-known polymers produced according to prior art:

1. The polymer products can be used in manufacturing absorbent materials where an extremely low content of residual monomers is demanded for toxicological reasons, e.g. in superabsorbers for the hygiene industry

(diapers, incontinence products), food industry (packagings), in soil improvers, etc..

2. The polymer products can also be used in the controlled release of other substances subsequently incorporated in the polymer or contained in the polymer to other bodies, e.g. in dosing drugs in human medicine, in dosing nutrients (fertilizer effect) to plants, insecticides and herbicides in aqueous media, preferably on large water surfaces, with no major quantities of toxicologically critical residual monomers invading the environment.
3. Non-crosslinked, water-soluble polymer products having low residual monomer content may also be used in such applications where low residual monomer levels are demanded for toxicological reasons, e.g. in drinking water treatment, when used as thickening agents in the food industry, in dosing of drugs, etc..

The incorporation of nutrients for plants, of herbicides, insecticides, disinfectants, drugs, antibacterial agents and other substances into the polymer product can be effected by directly adding these compounds to the monomer solution as long as the course of polymerization is not perturbed thereby. However, in case these substances do have an impact on the polymerization, their incorporation has to be effected not before during polymerization or after completed polymerization by including these substances in the ready-produced polymer gel according to e.g. DE 40 29 591, DE 40 29 592 or DE 40 29 593.

Examples

Absorptive capacity determination

1 g of polymer is added with stirring to a 250 ml beaker containing 200 ml of Fertilizer solution*. Following a stirring period of 15 minutes, the magnetic stirrer is turned off, and this is allowed to stand for 45 minutes. The content of the beaker then is poured over a screen having a mesh width of 0.3 mm, where the polymer swollen by the fertilizer solution remains on the screen. The amount of fertilizer solution absorbed by the polymer is calculated in ml/g of polymer from the difference between the 200 ml amount of solution originally employed and the amount of solution having passed the screen.

* Peters® Professional Fertilizer, Grace-Sierra Horticultural Products Comp., Pennsylvania, USA.

Determination of the residual monomer content

The residual monomer components acrylamide and acrylic acid are determined in aqueous extracts of the polymers using HPLC with internal standards.

Example 1

0.9 g of methylenebisacrylamide was initially dissolved in 275 g of water in a polymerization vessel and mixed with 301 g of acrylic acid. Thereafter, the monomer solution was neutralized with 168 g of sodium hydroxide solution (50%) and 118 g of ammonia (25%), cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions (1.0 g of sodium peroxodisulfate, 0.2 g of 2,2'-azobis(2-methylpropionamidine) dihydrochloride, each in 20 ml of water, and 0.05 g of Irgacure® 651 (photoinitiator, Ciba Geigy Company) in 2 g of acrylic acid), the

polymerization was initiated using UV light. Thorough mixing of the initiator solutions with the monomer solution is one precondition for homogeneous polymerization throughout the polymer block. The maximum temperature of 103°C (in a well-insulated polymerization vessel) was reached within 15 minutes. After completed polymerization, the polymer was heated at 160°C for 1.5 hours and milled to the desired grain fraction. A crosslinked acrylic acid homopolymer as sodium/ammonium salt had been formed. The screened grain fraction from 200 to 1000 μm was used for further investigations. The absorptive capacity for a 0.1% fertilizer solution was 103 ml/g, and the residual monomer content was 20 ppm of acrylic acid.

Example 2

Under similar conditions as in Example 1, 0.6 g of methylenebisacrylamide was dissolved in 275 g of water and mixed with 301 g of acrylic acid. Thereafter, the monomer solution was neutralized with 261 g of potassium hydroxide solution (50%) and 118 g of ammonia (25%), cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions as in Example 1, the polymerization was initiated using UV light. The maximum temperature of 102°C was reached within 10 minutes. After completed polymerization, the polymer was heated at 180°C for 1.5 hours and milled to the desired grain fraction. A crosslinked acrylic acid homopolymer as potassium/ammonium salt had been formed. The screened grain fraction from 200 to 1000 μm was used for further investigations. The absorptive capacity for a 0.1% fertilizer solution was 110 ml/g, and the residual monomer content was 12 ppm of acrylic acid.

Example 3

0.6 g of methylenebisacrylamide was initially dissolved in 290 g of water in a polymerization vessel and mixed with 208 g of acrylic acid and 223 g of acrylamide solution (40%). Thereafter, the monomer solution was neutralized with 180 g of potassium hydroxide solution (50%) and 39.3 g of ammonia (25%), cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions as in Example 1, the polymerization was initiated using UV light. The maximum temperature of 104°C was reached within 8 minutes. After completed polymerization, the polymer was heated at 160°C for 1.5 hours and milled to the desired grain fraction. A crosslinked acrylic acid/acrylamide copolymer as potassium/ammonium salt had been formed. The screened grain fraction from 200 to 1000 µm was used for further investigations. The absorptive capacity for a 0.1% fertilizer solution was 120 ml/g, and the residual monomer content was 10 ppm of acrylic acid and 10 ppm of acrylamide.

Example 4

Under similar conditions as in Example 3, a terpolymer of acrylamide, acrylic acid and acrylamido(2-methylpropane)sulfonic acid (AMPS) at a ratio of 50/49.3/0.7 mole-% was produced. 50% of the acrylic acid was neutralized with potassium hydroxide solution and 40% with ammonia (25%). After completed polymerization, the polymer was heated for 1.5 hours at 140°C and 160°C, respectively. The absorptive capacity for a 0.1% fertilizer solution was 110 and 108 ml/g, respectively, and the residual monomer content was 28 ppm of acrylic acid and 9 ppm of acrylamide or 15 ppm of acrylic acid and 7 ppm of acrylamide.

Example 5

0.6 g of methylenebisacrylamide was dissolved in 230 g of water in a polymerization vessel and mixed with 118.6 g of acrylic acid and 446.4 g of acrylamide (40%). Thereafter, the monomer solution was neutralized with 102.6 g of potassium hydroxide solution (50%) and 46.1 g of ammonia (25%), cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions according to Example 1, the polymerization was initiated using UV light. The maximum temperature of 102°C was reached within 8 minutes. After completed polymerization, the polymer was heated at 160°C for 1.5 hours and milled to the desired grain fraction. A crosslinked acrylic acid/acrylamide copolymer as potassium/ammonium salt had been formed. The absorptive capacity for a 0.1% fertilizer solution was 106 ml/g, and the residual monomer content was 15 ppm of acrylic acid and 10 ppm of acrylamide.

Examples 6 to 35

146.5 g of acrylic acid, 372 g of acrylamide solution (40%) and 6.9 g of AMPS were initially mixed in 230 g of water in a polymerization vessel. The monomer solution was added with varying amounts of various crosslinkers, so that polymers having varying crosslinking levels were formed. Methylenebisacrylamide (MBA), triallylamine (TAA) and trimethylolpropane (TMPTA) alone or in combination were used as crosslinkers. Thereafter, the monomer solution was neutralized either with 128.5 g of potassium hydroxide solution (45%) and 56 g of ammonia (25%) (Examples 6 to 14) or with 126 g of ammonia and with 84.2 g of ammonia (25%), respectively (Examples 15 to 35), so as to result in an overall neutralization level of 90% and 60%, respectively. The monomer solution was cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions ac-

Grain fractions of from 200 to 1000 μm were used for further investigations. Amounts of crosslinker, absorptive capacities and residual monomer levels can be inferred from the following Table.

Ex.	Amount crosslinker			Neutralization		Absorptive capacity 0.1 % Fertilizer soln.	Residual monomer	
	MBA	TMPTA	TAA	KOH	NH ₃		AcA	AcS
	(% rel. w.s.)			(%)		(ml/g)	(ppm)	
6	0.1			50	40	142	4	15
7	0.25			50	40	120	5	11
8	0.3			50	40	112	5	20
9	0.3			50	40	113	4	25
10	0.5			50	40	98	6	40
11		0.4		50	40	157	5	30
12		0.8		50	40	146	7	25
13	0.1	0.2		50	40	135	5	30
14	0.1		0.4	50	40	112	6	25
15	0.2			0	60	128	8	10
16	0.25			0	60	120	11	11
17	0.3			0	60	114	16	11
18	0.4			0	60	108	13	10
19	0.2	0.1		0	60	118	20	15
20	0.2	0.2		0	60	120	37	30
21	0.2	0.4		0	60	111	19	10
22	0.1		0.4	0	60	120	6	5
23	0.1		0.8	0	60	112	5	5
24	0.2		0.2	0	60	118	16	20
25	0.2		0.4	0	60	115	20	15
26	0.2			0	90	130	7	33
27	0.25			0	90	120	6	15
28	0.3			0	90	120	8	13
29	0.2	0.1		0	90	134	7	12
30	0.2	0.2		0	90	130	8	38
31	0.2	0.4		0	90	126	9	11
32	0.1		0.8	0	90	115	9	13
33	0.2		0.2	0	90	110	7	35
34	0.2		0.4	0	90	106	9	12
35	0.2		0.8	0	90	104	11	20

Example 36

The monomer solution according to Example 6 having 0.9 g of methylenebisacrylamide was neutralized with 128 g of potassium hydroxide solution (45%) to a neutralization level of 50%. Following addition of 25.1 g of ethanolamine, the monomer solution was cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions according to Example 1, the polymerization was initiated using UV light. The maximum temperature of 104°C was reached within 8 minutes. After completed polymerization, the polymer was heated at 160°C for 1.5 hours and milled to the desired grain fraction. The absorptive capacity for a 0.1% fertilizer solution was 48 ml/g, and the residual monomer content was 20 ppm of acrylic acid and 17 ppm of acrylamide.

Example 37

The monomer solution according to Example 6 having 0.9 g of methylenebisacrylamide was neutralized with 120 g of potassium hydroxide solution (45%) to a neutralization level of 50%. Following addition of 50.2 g of ethanolamine, the monomer solution was cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions according to Example 1, the polymerization was initiated using UV light. The maximum temperature of 104°C was reached within 6 minutes. After completed polymerization, the polymer was heated at 160°C for 1.5 hours and milled to the desired grain fraction. The absorptive capacity for a 0.1% fertilizer solution was 46 ml/g, and the residual monomer content was 20 ppm of acrylic acid and 11 ppm of acrylamide.

Example 38

148 g of acrylic acid, 372 g of acrylamide solution (40%), 0.6 g of methylenebisacrylamide, and 1.2 g of triallylamine were initially dissolved in 260 g of water in a polymerization vessel. Thereafter, the monomer solution was neutralized with 126 g of ammonia (25%) to a neutralization level of 90%. The monomer solution then was cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions (0.8 g of ABAH, 1.0 g of sodium peroxodisulfate, 0.2 g of hydrogen peroxide, and 0.05 g of ascorbic acid, each in 5 ml of water), the polymerization was initiated. The maximum temperature of 100°C was reached within 10 minutes. After completed polymerization, the polymer was heated at 140°C for 1.5 hours and milled to the desired grain fraction. A crosslinked acrylic acid/acrylamide copolymer as ammonium salt had been formed. The absorptive capacity for a 0.1% fertilizer solution was 132 ml/g, and the residual monomer content was 10 ppm of acrylamide and 25 ppm of acrylic acid.

Example 39

Initially, 146 g of acrylic acid, 372 g of acrylamide solution (40%) and 14 g of AMPS (50%) in 300 g of water were mixed in a polymerization vessel. Thereafter, the monomer solution was neutralized with 126 g of ammonia (25%) to a neutralization level of 90%. The monomer solution then was cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions according to Example 1, the polymerization was initiated using UV light. The maximum temperature of 100°C was reached within 10 minutes. After completed polymerization, the polymer was heated at 140°C for 1.5 hours and milled to the desired grain fraction. A high molecular weight, water-soluble acrylic acid/acrylamide copolymer with a residual monomer

content of 3 ppm of acrylic acid and 5 ppm of acrylamide had been formed. A 0.1% aqueous solution of this polymer had a Brookfield viscosity of 400 mPa·s.

Example 40

Initially, 146 g of acrylic acid was mixed with 493 g of water in a polymerization vessel. Thereafter, the monomer solution was neutralized with 168 g of ammonia (25%) to a neutralization level of 60%. The monomer solution then was cooled to 10°C and purged with nitrogen. Following addition of the initiator solutions according to Example 1, the polymerization was initiated using UV light. The maximum temperature of 102°C was reached within 10 minutes. After completed polymerization, the polymer was heated at 140°C for 1.5 hours and milled to the desired grain fraction. A high molecular weight, water-soluble acrylic acid polymer with a Brookfield viscosity of 240 mPa·s and a residual monomer content of 11 ppm of acrylic had been formed.

Example 41

Example 40 was repeated; however, the polymer was heated to 160°C instead of 140°C. The polymer product had a Brookfield viscosity of 350 mPa·s, and the residual monomer content was 18 ppm of acrylic acid.

Claims:

1. A process for producing water-soluble or water-swellaable synthetic polymer products by free-radical polymerization in aqueous solution of acrylic acid and/or acrylic acid derivatives partially or completely neutralized with basic nitrogen compounds, characterized in that exceedingly low residual monomer levels are achieved by subsequent heating of the polymer products at a temperature of from 120 to 240°C.
2. The process according to claim 1, characterized in that ammonia, ammonium hydroxide, hydroxylamine, alkanolamines, or alkylamines and/or mixtures thereof are used as nitrogen compound.
3. The process according to claims 1 and 2, characterized in that ammonia, ammonium hydroxide, mono- or diethanolamine are preferably used as nitrogen compound.
4. The process according to claims 1 to 3, characterized in that the acid monomer component is neutralized with said nitrogen compound up to a neutralization level of from 10 to 100%.
5. The process according to claims 1 to 4, characterized in that monomers based on acrylic acid, methacrylic acid or derivatives of these carboxylic acids are subjected to polymerization, preferably as homo- or copolymers of acrylic, methacrylic acid, acrylamidopropanesulfonic acid, alkali or ammonium salts of these carboxylic acids, of acryl- or methacrylamide and derivatives thereof, of vinylpyrrolidone, and as copoly-

mers of each other, or are used with other, only partially water-soluble monomers such as vinyl acetate.

6. The process according to claims 1 to 5, characterized in that at least one crosslinker based on a bi- or polyfunctional monomer is used in addition.
7. The process according to claims 1 to 6, characterized in that the polymer product is heated at a temperature of from 140 to 180°C.
8. The process according to claims 1 to 7, characterized in that polymer products having a content of residual monomer of less than 50 ppm, preferably less than 30 ppm are formed.
9. The process according to claims 1 to 8, characterized in that polymer products having a residual content of acrylamide of less than 10 ppm are formed.
10. Polymers based on acrylic acid and/or acrylic acid derivatives, obtained according to one or more of claims 1 to 9.
11. Use of the process products according to claims 1 to 9 for absorbing and/or retaining water and/or aqueous solutions, urine and body fluids, for subsequent controlled release of water and/or substances dissolved in aqueous media, for the manufacture of hygiene products, for potable water treatment, as thickening agents, as dispersants, and as flocculants for waste water treatment.

Abstract:

The invention relates to a process for producing water-soluble or water-swellaable polymer products from acrylic acid and/or acrylic acid derivatives partially or completely neutralized with nitrogen compounds and with exceedingly low levels of residual monomers, which process is characterized by subsequent heating of the polymer product at temperatures of from 120 to 240°C. The polymers produced accordingly are suitable for use as flocculants, dispersants and absorbers.

Declaration and Power of Attorney for Patent Application

Erklärung für Patentanmeldungen mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt

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I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

METHOD FOR PRODUCING WATER-SOLUBLE
OR WATER-SWELLABLE POLYMERIZATES WITH
A VERY LOW RESIDUAL MONOMER CONTENT,
PRODUCTS PRODUCED ACCORDING TO THIS
METHOD AND THE USE THEREOF

deren Beschreibung

the specification of which

☐ ist beigefügt

☐ is attached hereto.

☐ wurde angemeldet am _____

☒ was filed on 13 November 1998

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PCT/EP98/07290 13 November 1998
(Application No.) (Filing Date)
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Priority Not Claimed
Priorität nicht beansprucht

25 November 1997 ☐
(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

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German Language Declaration

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Staatsangehörigkeit	Citizenship
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Vor- und Zuname des zweiten Miterfinders (falls zutreffend)	Full name of second joint inventor, if any
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